

UNCLASSIFIED

405 893

AD

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

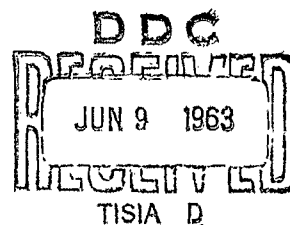
NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

63-3-5

405893

405 893

**CENTRAL
RESEARCH
LABORATORY**



THE BORDEN CHEMICAL COMPANY

A Division of The Borden Company

GODFREY AVENUE AND LANGDON STREET

P. O. BOX 9524, PHILADELPHIA 24, PA.

Study Leading to the
Development of

REINFORCED HIGH TEMPERATURE ELASTOMERS

K.C. Tsou
S.J. Makower
R.N. Goldey
B.D. Halpern

by

Central Research Laboratory
The Borden Chemical Company
Division of the Borden Company
Philadelphia 24, Pennsylvania

QUARTERLY PROGRESS REPORT NO. 2

1 January 1963 - 31 March 1963

CONTRACT NO. DA-36-034-AMC-3791-W

U. S. Army Ordnance District, St. Louis
Rock Island Arsenal
Rock Island, Ill.

	<u>Page No.</u>
<u>TABLE OF CONTENTS</u>	
PREFACE	iii
OBJECTIVE	ii
SUMMARY	i
INTRODUCTION	1
RESULTS & DISCUSSION	2
1. Comparison of Trimethylsilyl and Triphenylsilyl Modified Fillers	2
2. Influence of Loading of Triphenylsilyl Modified Filler on Silicone Rubber	6
3. Investigation of Non-Reinforcing Filler	9
4. Evaluation of Baymal Collodial Alumina	25
5. Investigation of Vinylated Fillers	27
6. Investigation of Titanium Compounds	29
7. Other Additives	30

<u>INDEX OF FIGURES</u>	
Fig. 1 - Change of Tensile and Elongation of Silicone Rubber with Loading of Ph_3SiCl Modified Hi-Sil	8
Fig. 2 - Change of Tensile and Elongation with Loading of Neo Novacite Filler	10
Fig. 3 - Change of Tensile and Elongation with Loading of Neo-Novacite	11
Fig. 4 - Change of Tensile at 500° F. With Time of Aging at 500° F.	12
Fig. 5 - Change of Elongation at 500° F. with Time of Aging at 500° F.	13
Fig. 6 - Effect of Aging at 500° F. of Silicone Rubber Loaded with 20 Parts Non-reinforcing Filler	19
Fig. 7 - Effect of Aging at 500° F. of Silicon Rubber Loaded with 40 Parts Non-reinforcing filler	20
Fig. 8 - Effect of Loading of Non-Reinforcing Fillers Tensile and Elongation at 72°F. of Unaged Samples	21
Fig. 9 - Tensile and Elongation Data Asbestine 3X	22
Fig.10 - Tensile and Elongation Data Asbestine 625	23
Fig.11 - Tensile and Elongation Data - Neo Novacite	24

References

PREFACE

This report was prepared by Central Research Laboratory of the Borden Chemical Company under U. S. Army Contract No. DA-36-034-AMC-3791-W and is a continuation of effort of Contract No. DA-36-034-ORD-3523-RD. The work was performed for Rock Island Arsenal, Rock Island, Illinois. Dr. Z. Ossefort acted as Project Officer.

The period covered is from January 1, 1963 to March 31, 1963.

Personnel assigned to this project are Dr. S. J. Makower (on leave of absence in March), Mr. R. N. Goldey and Dr. K. C. Tsou who serves as project director. Mr. R. Trickey assists in the physical testing and electron microscopic study, under the supervision of Dr. G. Kitazawa.

Approved by: Dr. B. D. Halpern
Research Director
Central Research Laboratory
The Borden Chemical Company

OBJECTIVE

To improve the performance of elastomers at high temperature by the use of chemically modified fillers, and to achieve a better understanding of filler-rubber interaction in these systems.

SUMMARY

A comparison of trimethylsilyl and triphenylsilyl modified silicas indicate that the trimethylsilyl modified filler is more suitable for higher tensiles at high temperature without sacrificing room temperature tensile and elastic property.

A comprehensive study has been carried out with various non-reinforcing fillers to determine their relative usefulness for improving high temperature performance. Asbestine 3-X , a fibrous grade of talc., was chosen as the best non-reinforcing filler to obtain high tensile at 500°F. after aging at the same temperature.

INTRODUCTION

1.

In this period work has been continued along the lines outlined in the previous report. A comparison of various non-reinforcing fillers such as asbestos, Baymal alumina, etc. have been carried out. The preparation of trialkyl substituted filler has been continued, and attempts to further understand the thermal effect on these fillers have been made.

RESULTS & DISCUSSION

1. Comparison of Trimethylsilyl and Triphenylsilyl Modified Fillers:

As mentioned in the earlier reports, triphenylsilyl modified silicas have been prepared in order to take advantage of both the thermal stability of the phenyl group and the possible chain blocking of the triphenylsilyl group in the rearrangement of the siloxane bond of the silicone rubber during thermal degradation. Similarly, the trimethylsilyl modified silica should undergo the expected rearrangement and impart an improvement in the high temperature tensile strength when milled into silicone rubber. Several such silicon rubber samples containing silica modified with trimethylchlorosilane were therefore prepared. Their effects on the performance of the silicone rubber at high temperature were compared with the triphenylsilyl modified fillers.

In general, the preparation of the trimethylsilyl silica was easier than the preparation of the triphenylsilyl silica. Almost theoretical amount of Si-OH available were reacted as seen in Table I. The ease of reaction can be attributed to both less steric hindrance of the trimethylsilyl group than the triphenylsilyl group, and the reactivity of the chlorine in the trimethyl compound. Determination of the amount of chemically modified silica has been made by combustion of the organic groups. A comparison of combustibles alone can be misleading in comparing the extent of modification effectuated by triphenylchlorosilane vs. trimethylchlorosilane. Because of the lower molecular weight of the organic (combustible) portion of the trimethylsilyl group, approximately six times as much combustibles

must be present on a triphenylsilyl filler for an equal degree of reactivity, assuming the Si remains as ash. If the Si of this modifier also volatilizes only 3.5 times more combustibles occurs in the case of the triphenylsilyl modification.

Table I Per Cent Theoretical Combustible Content:
Trimethylsilyl vs. Triphenylsilyl Modified Fillers
on Hi Sil x 303

<u>Filler No.</u>	<u>Modifier</u>	<u>Solvent</u>	<u>% Combustibles^d</u>	<u>% of Theory^e</u>
253-75	Me ₃ SiCl	T.H.F. ^a	7.7%	108.7%
253-81	Me ₃ SiCl	D.M.A. ^b	6.9%	97.4%
253-94	Me ₃ SiCl	D.M.A.	6.67%	94.1%
305-67	φ ₃ SiCl	D.M.F. ^c	9.26%	21.6%
305-89	SiCl ₄ + Liφ	Ether	10.5%	24.5%
305-106	φ ₃ SiCl	D.M.A.	10.37%	24.2%

a/ Tetrahydrofuran;

b/ Dimethylacetamide

c/ Dimethylformamide

d/ Determined by ignition in a muffle furnace at 700°C.

e/ Theoretical value for Me₃Si on Hi-Sil x-303 (4% bound water) 7.08%;
for φ₃Si, 42.8%.

In the previous report, it was shown that increase of TMS filler (trimethylsilyl modified) caused an increase in room temperature as well as high temperature tensile strength, but lowered the elongation. On the other hand, continuous aging at 500° or 600° F. for 48 hours resulted in higher tensile strength. The initial lowering of tensile at 500°F. can be overcome only slightly by a higher loading of the modified filler (e.g., from 35 parts to 45 parts, from 148 psi to 232 psi - see Table II). A combination of TMS modified filler and a non-reinforcing filler, however, gave reasonably good tensile strength at 500° F. even after 142 hours aging at 500° F. For long term service purpose, this sample (305-115-H) represents one of the best improvements to date. All other samples, including the Rock Island formula, turned brittle and lost elasticity after this prolonged treatment. Details of non-reinforcing filler work, will be discussed later, but the comparison of these three samples is summarized below in Table II.

Table II

<u>Sample No.</u>	<u>Description</u>	<u>Test</u> <u>Temp. °F</u>	<u>Tensile</u> <u>(psi)</u>	<u>Elongation</u> <u>(%)</u>	<u>50%</u> <u>Modulus</u>	<u>Hard-</u> <u>ness</u> <u>Shore A</u>
253-92-3	Silastic 440 + 35 pts.	72	647	1035	33	47
	TMS filler ^a	500	148	328	33	57
	24 hr. aging at 600°F	500	184	105	85	65
	48 hr. aging at 600°F	500	297	72	101	78
305-109-A	Silastic 440 + 45 pts	72	818	741	73	53
	TSM filler	500	232	239	34	
	24 hr. aging at 500°F	500	323	100	112	81
305-115-H	Silastic 440 + 35 pts	72	808	725	71	55
	TMS filler, 20 pts					
	N.N.b	500	247 ^c	235 ^c	71	
	48 hr. aging, 500°F	500	228	132	108	62
	142 Hr. aging at 500°F	500	262	100	151	67

a) TMS filler - Me_3Si - modified Hi-Sil

b) N.N. - NeoNovacite

c) Rock Island formula gives 300 p.s.i. and 100% under this condition.

2. Influence of Loading of Triphenylsilyl Modified Filler on
Silicone Rubber

A large batch of Hi-Sil x303 was modified with triphenylchlorosilane in order to check the influence of the loading of filler upon the physical properties of the rubber. Samples were compounded with 35, 50 and 65 parts of filler and with 100 parts of polydimethyl (phenyl vinyl) siloxane, SE-54. The milling with the modified filler even at the high filler level was good. Fig. 1 shows the change of the physical properties with the loading. At room temperature both the tensile as well as the elongation decreased with loading. However, at 500°F. the elongation decreased while the tensile increased. Aging caused a decrease of the tensile and elongation at 35 and 50 pts. of filler. At 65 pts. the elongation decreased but the tensile increased. The decrease in tensile is quite in contrast to the effect of trimethyl filler where a higher loading increases the tensile strength.

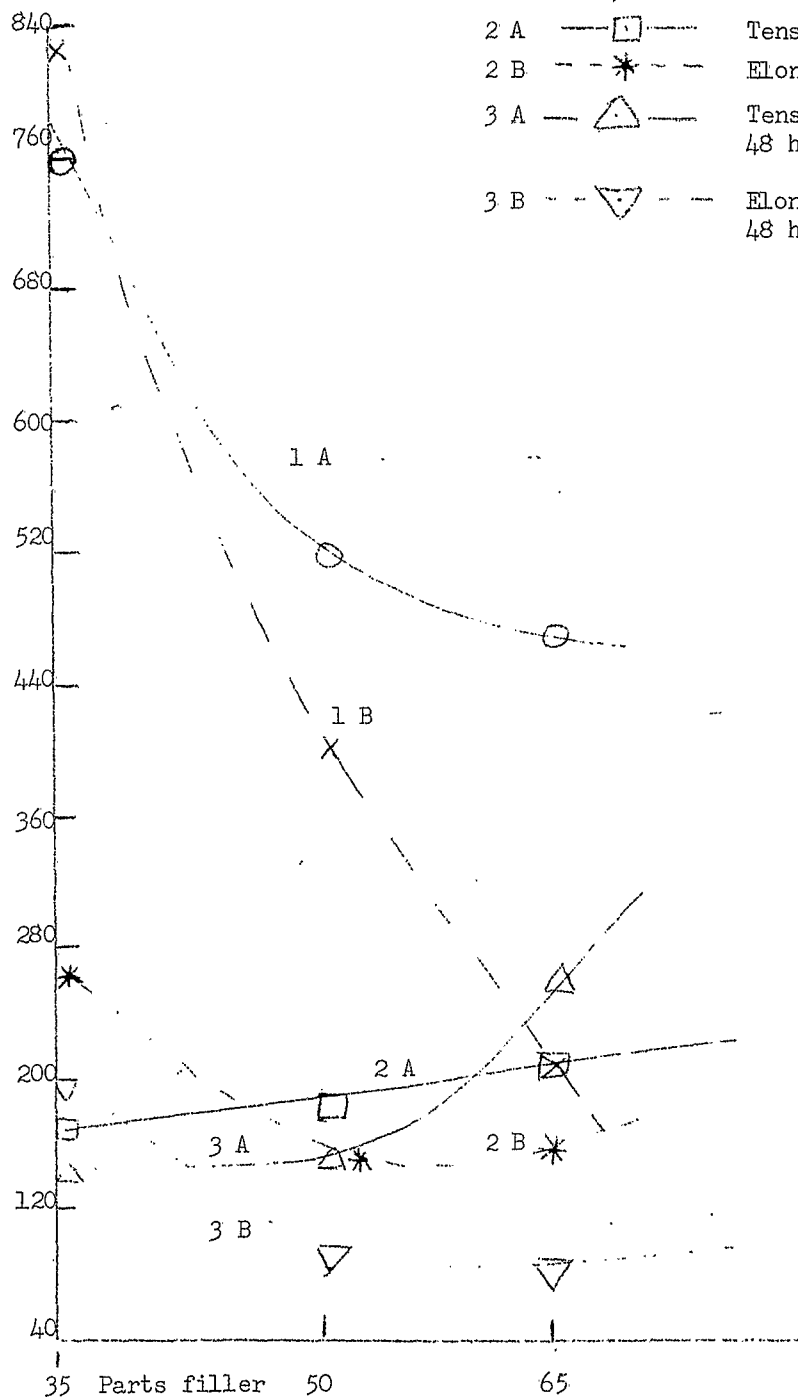
Table III Effect of Loading Upon Physical Properties of
Rubber Milled with Triphenylsilyl Modified Filler

Sample No.	Description	Test Temp.	Tens- ile (p.s.i.)	Elong. (%)	50% Modulus	(A-2 Duro.) Hardness
305-115-E	SE-54, + 35 pts.					
	Ph ₃ SiCl mod. Hi-Sil	72	762	830	54	56
		500	172	245	44	
	Aged 48 hrs., 500°F.	500	148	177	48	56
305-115-F	SE-54 + 50 pts.					
	Ph ₃ SiCl mod. Hi-Sil.	72	520	405	98	58
		500	185	168	67	
	Aged 48 hrs., 500°F.	500	162	101	94	65
305-115-G	SE-54 + 65 pts.					
	Ph ₃ SiCl mod. Hi-Sil	72	465	205	208	71
		500	207	146	111	
	Aged 48 hrs., 500°F.	500	249	74	188	80
	Aged 142 hrs. 500°F.	500	314	57		83

Fig. 1. - Change of Tensile and Elongation of Silicone Rubber with Loading
of Ph_3SiCl Modified Hi-Sil

Tensile (psi)
Elong. %

- | | | |
|-----|---------|---|
| 1 A | —○— | Tensile at room temp. |
| 1B | ---X--- | Elongation at room temp. |
| 2 A | —□— | Tensile at 500° F. |
| 2 B | ---*--- | Elongation at 500° F. |
| 3 A | —△— | Tensile at 500° F. after
48 hrs. aging at 500° F. |
| 3 B | ---▽--- | Elongation at 500° F. after
48 hrs. aging at 500° F. |



3. Investigation of Non-Reinforcing Filler

9.

During a recent discussion with Rock Island Laboratory we concluded that fibrous fillers might offer a decided improvement in high temperature strength. Support for this approach is found in the Air Force Work using pyrolyzed carbonaceous fillers to increase the high temperature performance of the fluorocarbons and butyl rubbers. Since the use of non-reinforcing fillers in combination with reinforcing fillers in order to improve the milling and shelf-aging life of silicone rubbers, has been known for some time, a series of compounds was prepared in order to check the influence of a non-reinforcing filler at different concentrations upon the heat stability of the rubber. A high molecular weight polydimethyl (vinyl) siloxane and a polydimethyl (phenyl vinyl) siloxane were used. Neo-Novacite was added at 0.20 and higher levels, Quso 1841 was used as the reinforcing filler. As shown in Fig. 2, when the tensile passed interestingly through a minimum in both room temperature and high temperature, the elongation passed at the same time through a maximum. At higher loading of SE-33 with Neo-Novacite an increase of the tensile and elongation over the samples without the non-reinforcing filler was observed. However, the aging of the samples at 500° F. caused a decrease of the tensile while no change was observed when SE-54 was used. Although increased loadings of filler do not markedly improve physical properties measured at room temperature, higher loadings of the so-called non-reinforcing filler were found to confer improved tensile strength at 500° F. both on aged and unaged samples (Fig. 4,5). It was therefore decided to make a comprehensive study of several non-reinforcing fillers.

Fig. 2 - Change of Tensile and Elongation with Loading of Neo Novacite Filler

10.

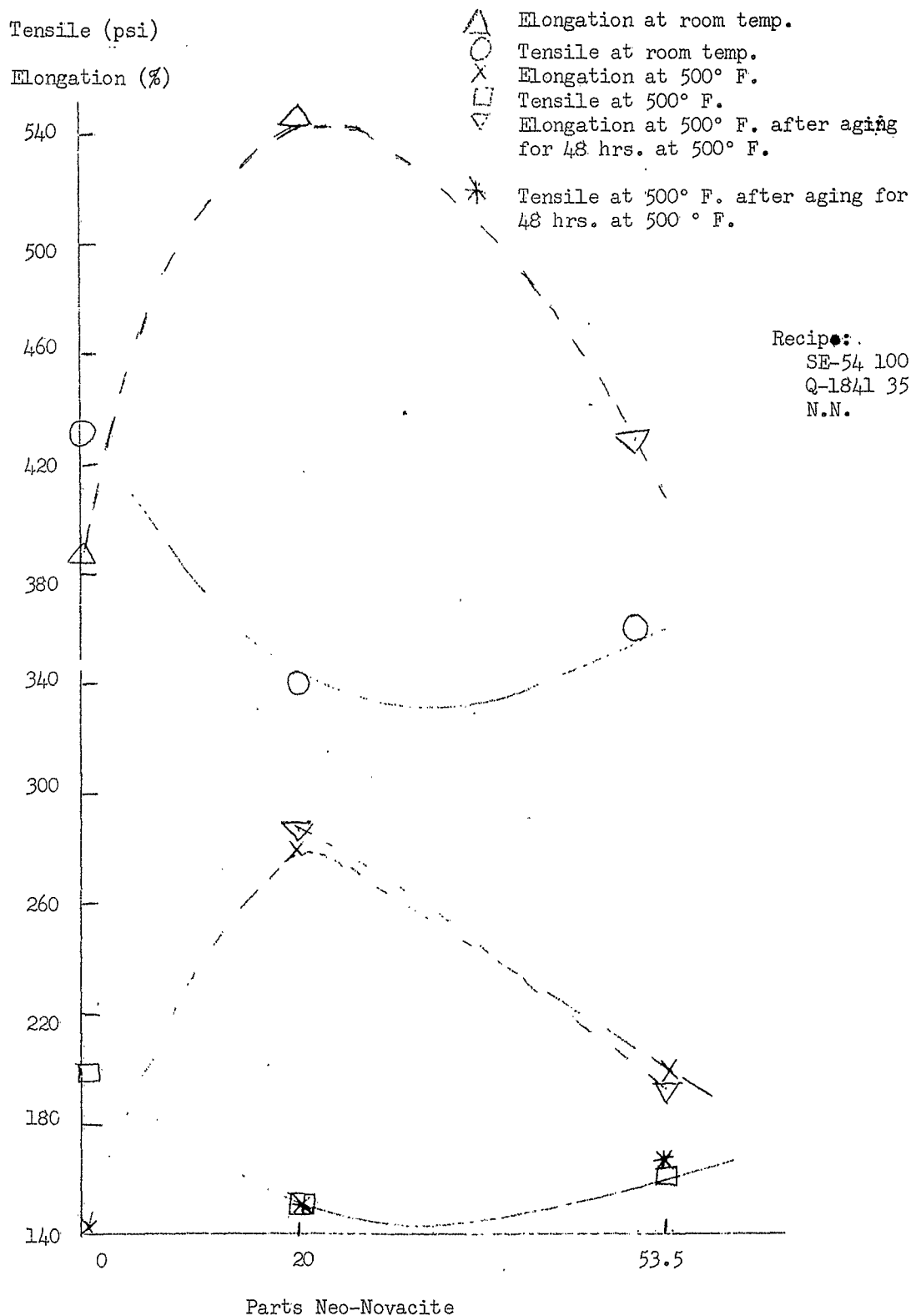


Fig. 3 - Change of Tensile and Elongation with Loading of Neo-Novacite

Recipe: SE-33 100
 Q-1841 35
 N.N. varied

Tensile (psi)

Elong. (%)

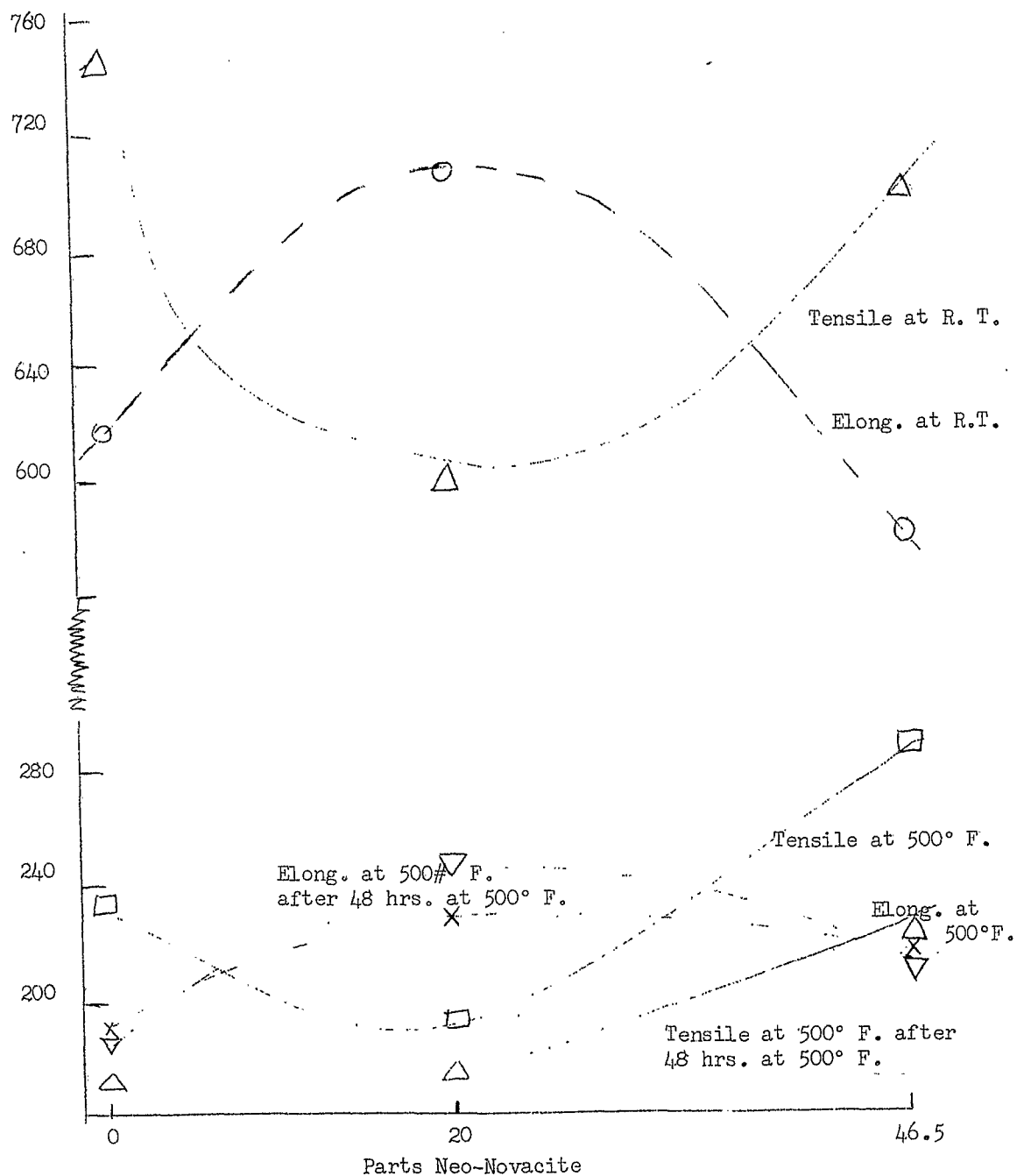
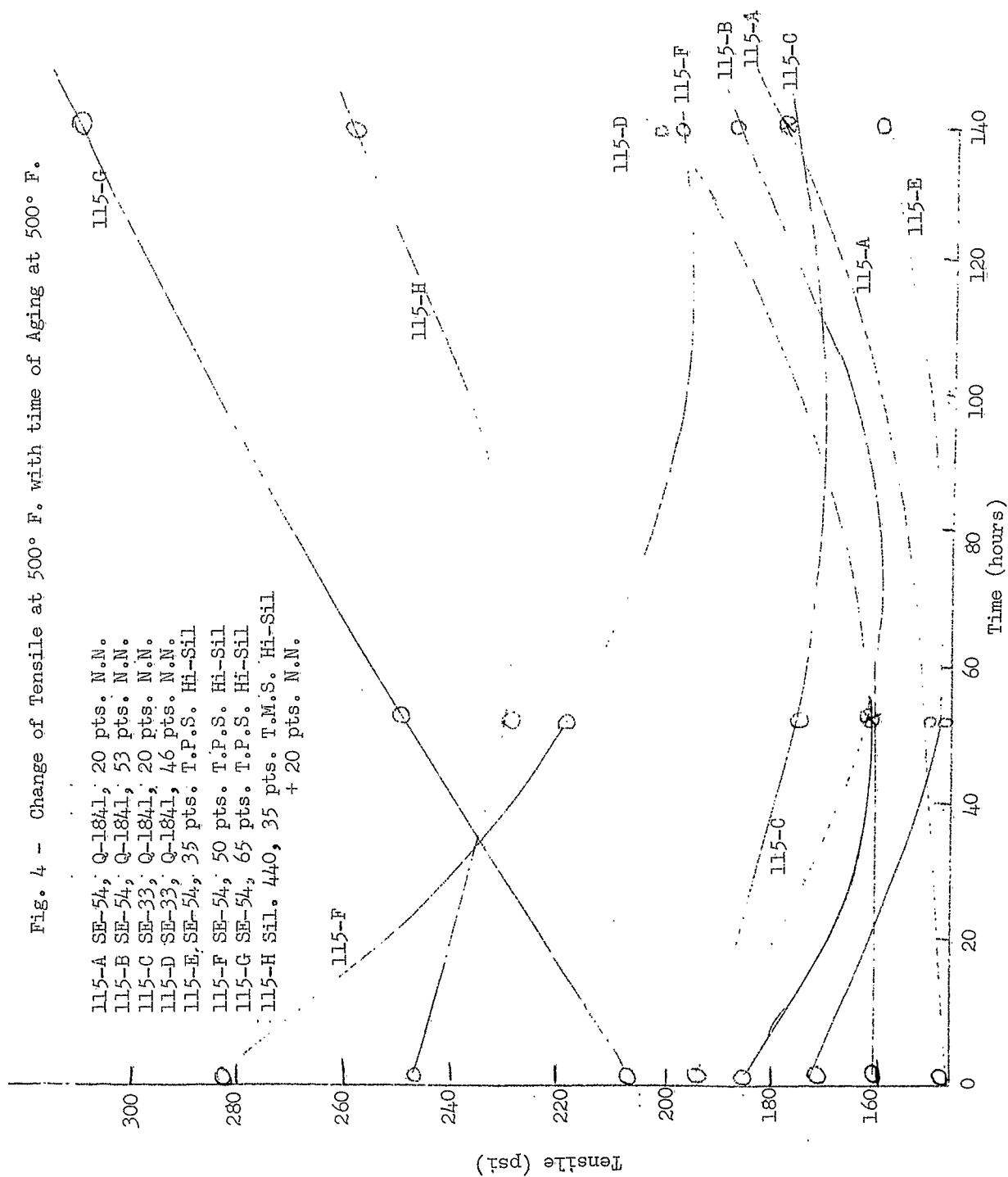
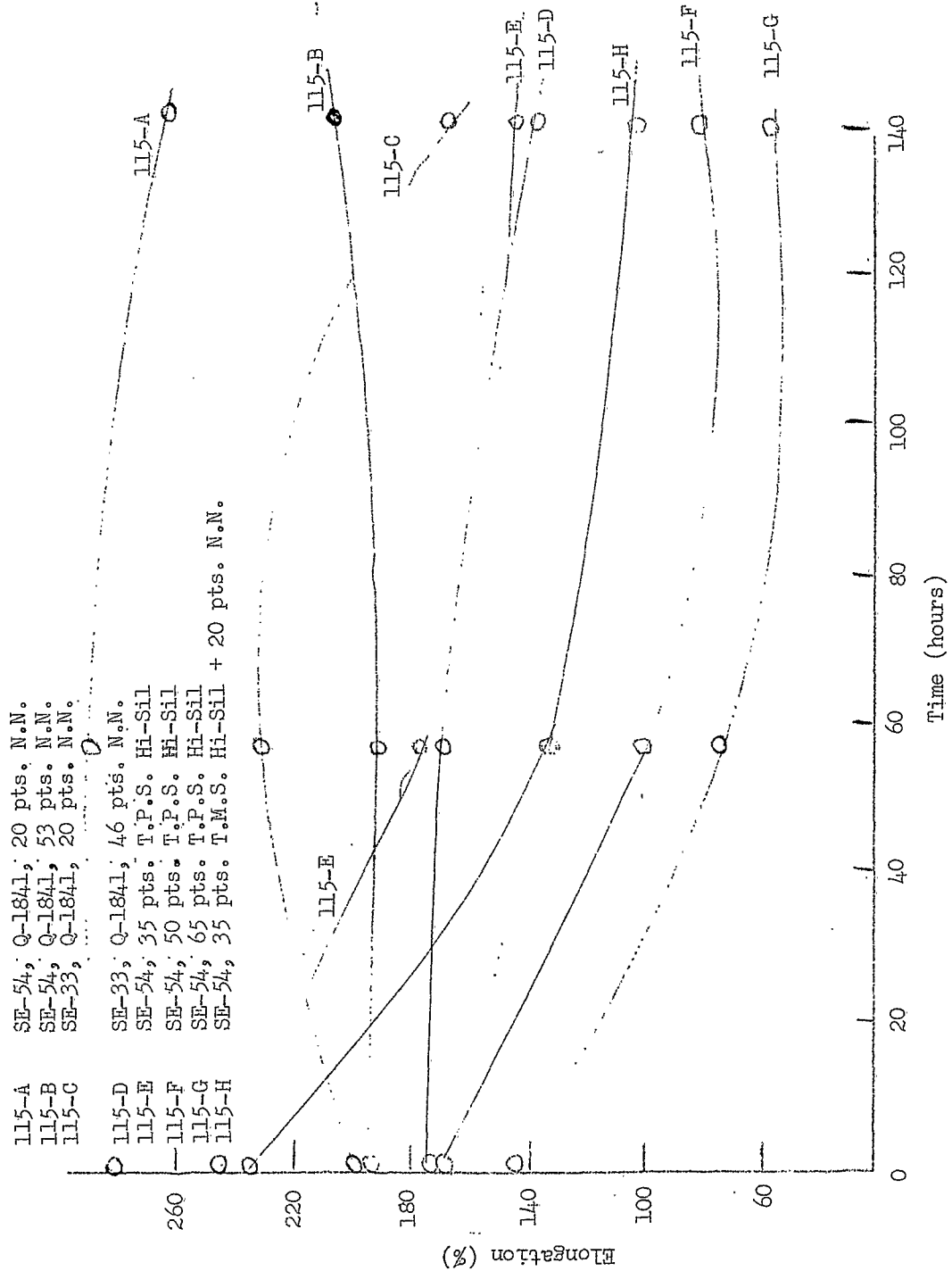


Fig. 4 - Change of Tensile at 500° F. with time of Aging at 500° F.



6)

Fig. 5 - Change of Elongation at 500° F. with Time of Aging at 500° F.



Using a standard formula of 100 parts SE-33 rubber, 35 parts Quso 1841 silica, 2 parts Fe_2O_3 , and 2 parts Cadox TS-50, loadings of 10, 20 and 40 parts each of Neo-Novacite, Asbestos Floats 7TFl, Asbestine 625 were milled. The data are shown in Table V. As shown in Figs. 6 and 7, Asbestine 3X shows consistently higher tensiles at 500° F., particularly after aging.

As high tensile strength is obtained, there is a loss of elasticity. With 40 parts Asbestine 3X, aged 48 hours at 500° F., an average tensile of 337 psi at 500° F. was obtained, with an elongation of 93% and a Shore A--2 Durometer Hardness of 82. This represents the onset of brittleness and it would seem that higher loadings aged for 48 hours would become excessively brittle. In contrast, when asbestos floats 7TFl were used, only 20 parts aged for 24 hours at 500° F. showed a tensile of 200 psi, an elongation of only 71%, and a hardness of 87. The milling of 40 parts 7TFl gave a material so brittle that it was not submitted for physical testing. Thus, the use of Asbestine 3X permits relatively high loadings of filler, gives tensile reinforcement, and introduces only a limited degree of brittleness.

For a study of this type, where large amounts of material are milled, it did not appear feasible to use modified silica as the reinforcing filler because of the quantities involved. However, we did make one milling (253-110-3) where 40 parts of a trimethylchlorosilane-modified filler was milled with 20 parts of Asbestine 3X into SE-33 rubber. The results are the best we have yet obtained. At room

temperature, a tensile of 870 psi and an elongation of 475% was obtained. At 500° F. tensile increased from 278 psi unaged to 352 psi after 48 hours aging, while elongation went from 142% to 99%. Hardness of the 48 hour aged sample was only 76. Further work along these lines is planned.

Asbestine is a product of International Talc Co., Inc. and is described as a magnesium silicate talc. Asbestine is marketed primarily as an inert extender for the paint industry. Asbestine 625 is a platey talc having high oil absorption and a small particle size (100% passing 325 mesh sieve). This sample was originally furnished by the supplier in answer to our request for a talc having maximum surface area. Asbestine 3X, supplied to us initially by Rock Island Arsenal, is a more fibrous material, having a slightly larger particle size (and presumably a smaller surface area.) Asbestine 3X is described as having medium oil absorption, and 98.5% passing 325 mesh sieve. In view of the data showing the 3X grade to give a higher tensile strength, we may conclude that surface area is not the governing variable in determining the effect of Asbestine, but that fibrous nature of the material is probably of most importance. The fact that tensile at room temperature is not improved by Asbestine 3X must also be considered.

Talc is closely related to asbestos. The formula for talc is given as $3 \text{ MgO} \cdot 4 \text{ SiO}_2 \cdot \text{H}_2\text{O}$, and for serpentine asbestos $3 \text{ MgO} \cdot 2 \text{ SiO}_2 \cdot 2 \text{ H}_2\text{O}$. The chemical content of Asbestine also includes 2.7-8.0% CaO, 0.10-0.30% Fe_2O_3 , 0.85-4.7% Al_2O_3 , and 0.3-2% CO_2 . In view of the known degradative effect of ionic materials, it is difficult to

Table IV Evaluation of Non-Reinforcing Fillers

Sample No. 305-	Description	Test Temp.	Tensile psi	Elong- ation %	50% Modu- lus	Hardness
123-A	SE-33 + 35 pts. Quso 1841/a (control)	72	654	700	82	56
	SE-33 + 35 pts. Quso 1841 (control)	500	189	184	78	-
	Aged 24 hrs. at 500°	500	170	173	76	59.5
	Aged 48 hrs. at 500°	500	197	193	82	61
123-1-B	Control + 10 parts Neo- Novacite /b	72	688	539	74	58
		500	245	203	78	-
	Aged 24 hrs. at 500°	500	214	203	66	59.5
	Aged 48 hrs. at 500°	500	219	201	72	60
123-1-C	Control + 20 parts Neo- Novacite	72	635	484	104	59.5
	Control + 20 parts Neo- Novacite	500	221	169	94	-
	Aged 24 hrs. at 500°	500	220	187	88	63
	Aged 48 hrs. at 500°	500	230	180	93	63.5
123-1-D	Control + 40 parts Neo- Novacite	72	639	470	102	60
	Control + 40 parts Neo- Novacite	500	229	177	91	-
	Aged 24 hrs. at 500°	500	239	191	89	63
	Aged 48 hrs. at 500°	500	253	195	93	64.5
123-2B	Control + 10 Parts Asb. 3X /c	72	663	577	98	59.5
	" " " "	500	241	193	81	-
	Aged 24 hrs. at 500°	500	230	178	89	61
	Aged 48 hrs. at 500°	500	227	182	87	63.5
123-2C	Control + 20 parts Asb. 3X	72	627	516	119	63
	" " " "	500	220	173	90	-
	Aged 24 hrs. at 500°	500	241	161	110	68
	Aged 48 hrs. at 500°	500	256	149	122	70.5
123-2D	Control + 40 parts Asb. 3X	72	549	362	182	66
	" " " "	500	287	148	133	-
	Aged 24 hrs. at 500°	500	291	124	167	75.5
	Aged 48 hrs. at 500°	500	337	93	230	82

TABLE CONTINUED ON FOLLOWING SHEET

TABLE IV (Continued)

Sample No. 305-	Description	Test Temp.	Tensile psi	Elong- ation %	50% Modu- lus	Hardness
123-3B	Control + 10 parts Asb. 625 °	72	662	538	81	55.5
	" " "	500	241	206	72	-
	Aged 24 hrs. at 500°	500	227	210	68	59.5
	Aged 48 hrs. at 500°	500	222	196	71	59
123-3C	Control + 20 parts Asb. 625	72	693	522	91	59
	" " "	500	226	179	83	-
	Aged 24 hrs. at 500°	500	230	168	76	63
	Aged 48 hrs. at 500°	500	123	146	95	64.5
123-3D	Control + 40 parts Asb. 625 °	72	643	363	117	62.5
	" " "	500	725	177	87	-
	Aged 24 hrs. at 500°	500	259	135	113	68
	Aged 48 hrs. at 500°	500	295	127	139	74
123-4B	Control + 10 parts Asbestos ^d					
	Floats	72	675	663	82	56.5
	Control + 10 parts Asbestos					
	Floats	500	215	207	76	-
	Aged 24 hrs. at 500°	500	227	136	125	70
123-4C	Control + 20 parts Asbestos					
	Floats	72	649	596	86	58
	Control + 20 parts Asbestos					
	Floats	500	200	179	78	-
	Aged 24 hrs. at 500°	500	200	71	176	87
123-4D	Control + 40 pars Asb. Floats		(very stiff - not tested)			
123-5B	Control + 10 Parts TiO ₂	72	686	620	95	57.5
	" " "	500	217	192	78	-
	Aged 24 hrs. at 500°	500	208	217	68	59.5
	Aged 48 hrs. at 500°	500	219	200	79	62
253-110-3	Se-33 + 40 parts 253-108 filler (T.M.S.-modified Quso) +					
	20 parts	72	870	475	129	62.5
	Asb. 3X	500	278	142	120	-
	Aged 24 hrs. at 500°	500	308	118	145	72
	Aged 48 hrs. at 500°	500	352	99	202	76

CONTINUED

Table IV (Continued)

-
- a) From Philadelphia Quartz Co., Philadelphia, Pa.
 - b) From Malvern Mineral Company, P. O. Box 1246, Hot Spring, Arkansas
 - c) From International Talc. Co., N. Y.
 - d) From Johns-Manville Co., Mansville, N. J.
-

(understand the benefit to be obtained by introducing such a mass of metallic impurities into the silicone rubber. Apparently, however, the talc is sufficiently stabilized that no harmful ionic degradation of the silicone rubber occurs, even at 500° F.

Fig. 6 - Effect of Aging at 500° F. of Silicone Rubber loaded with 20 Parts Non-Reinforcing Filler

19.

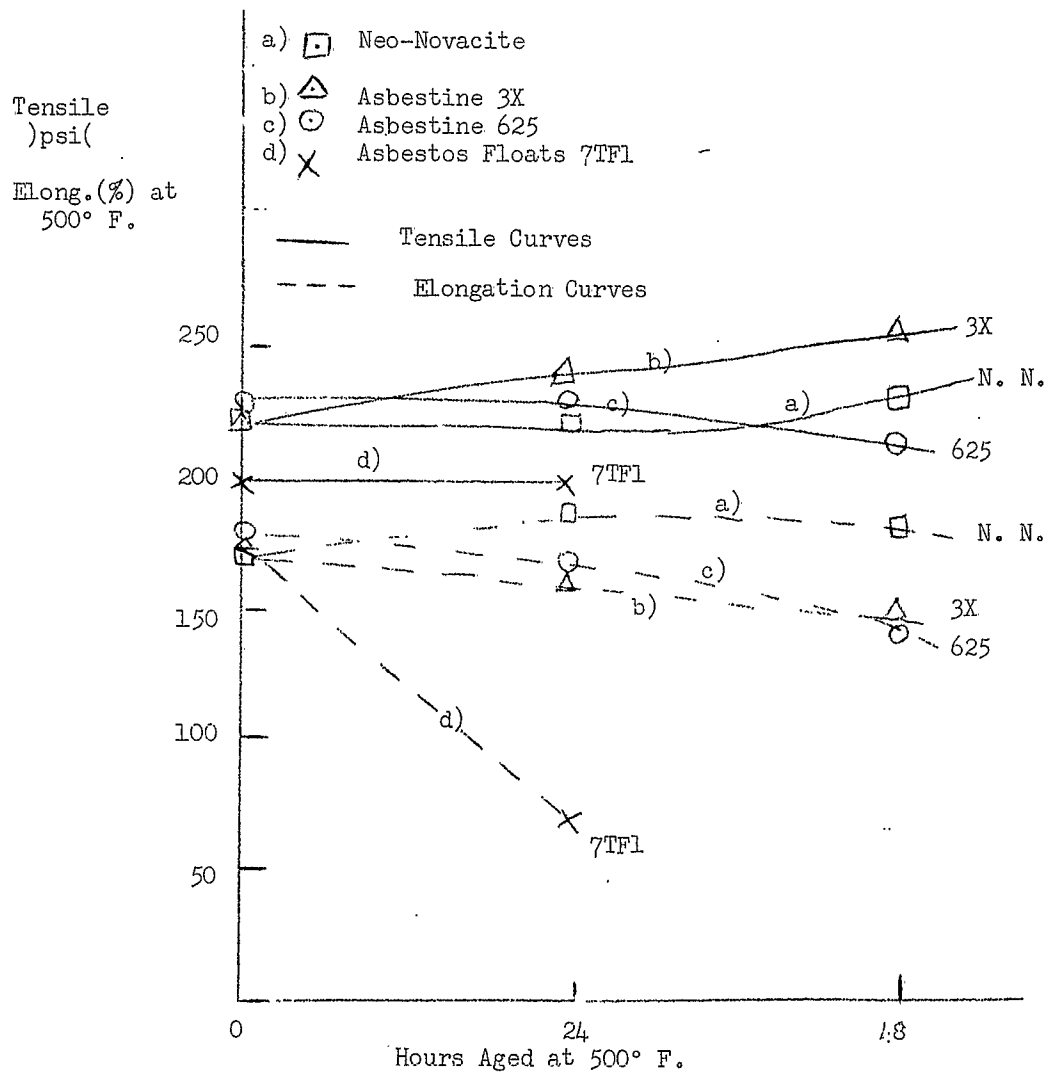


Figure 7 - Effect of Aging at 500° F. of Silicon Rubber Loaded with 40 parts Non-reinforcing Filler

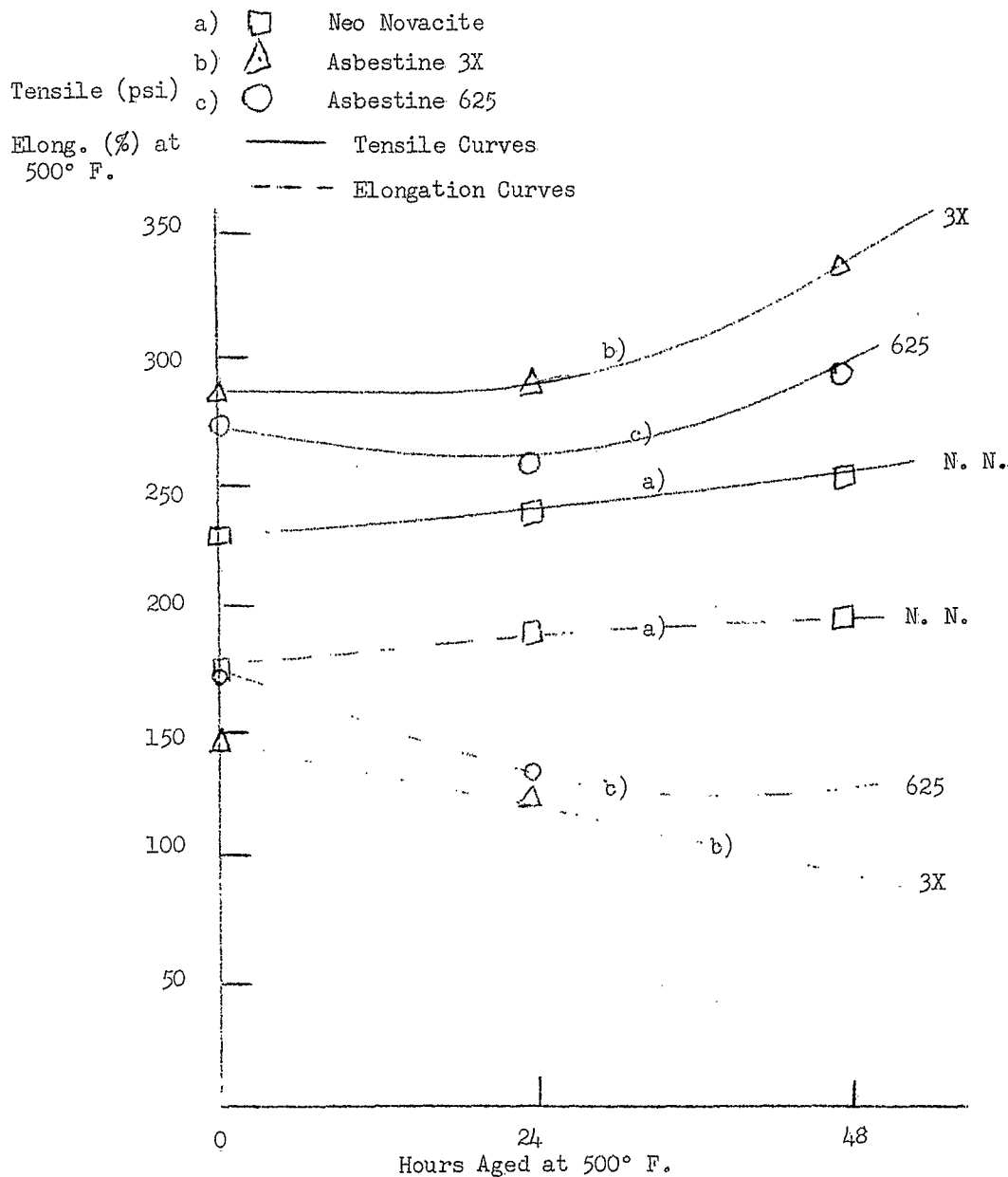


Fig. 8 - Effect of Loading of Non-Reinforcing Fillers
Tensile and Elongation at 72° F. of Unaged
Samples

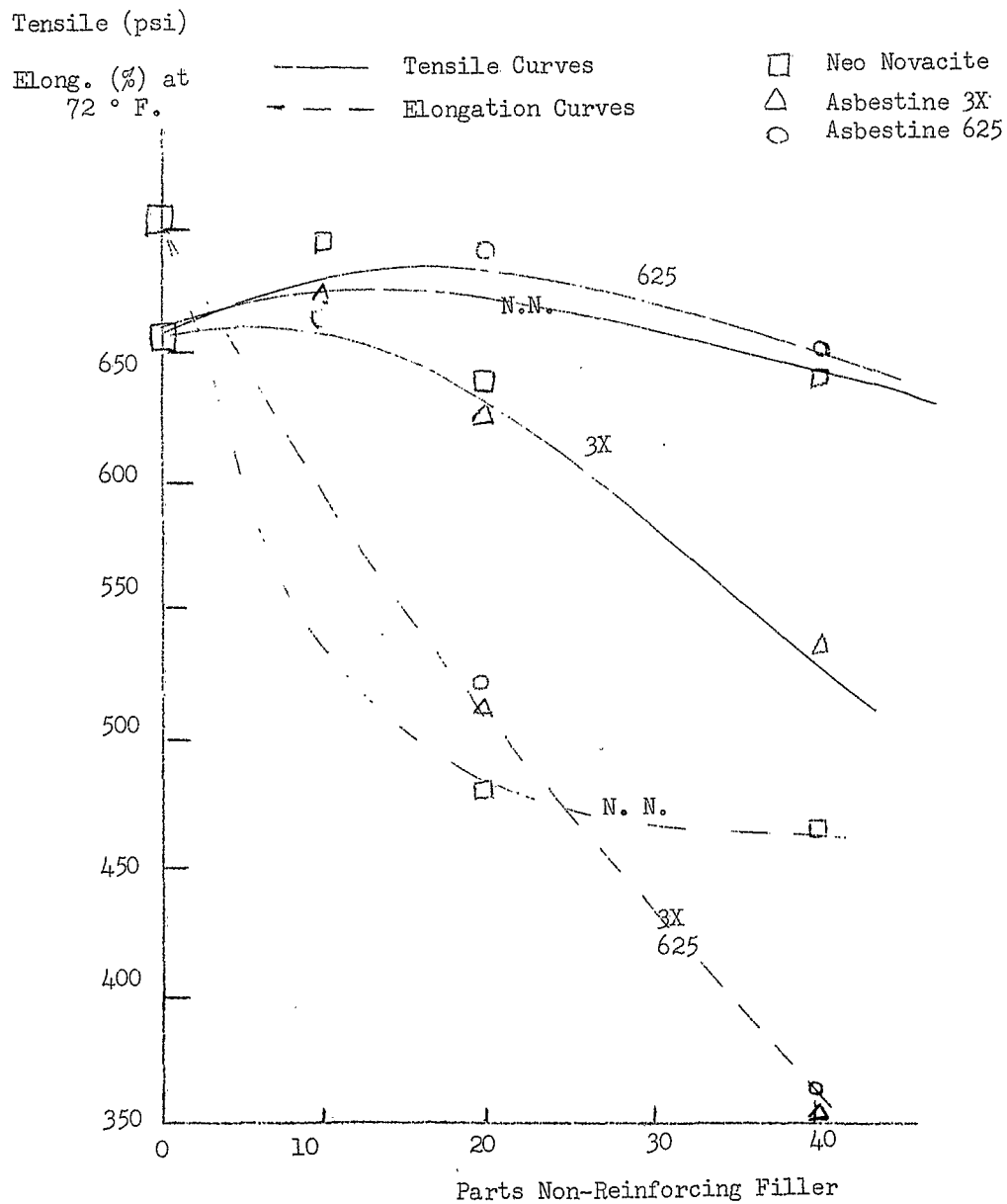


Fig. 9 - Tensile and Elongation Data
Asbestine 3X

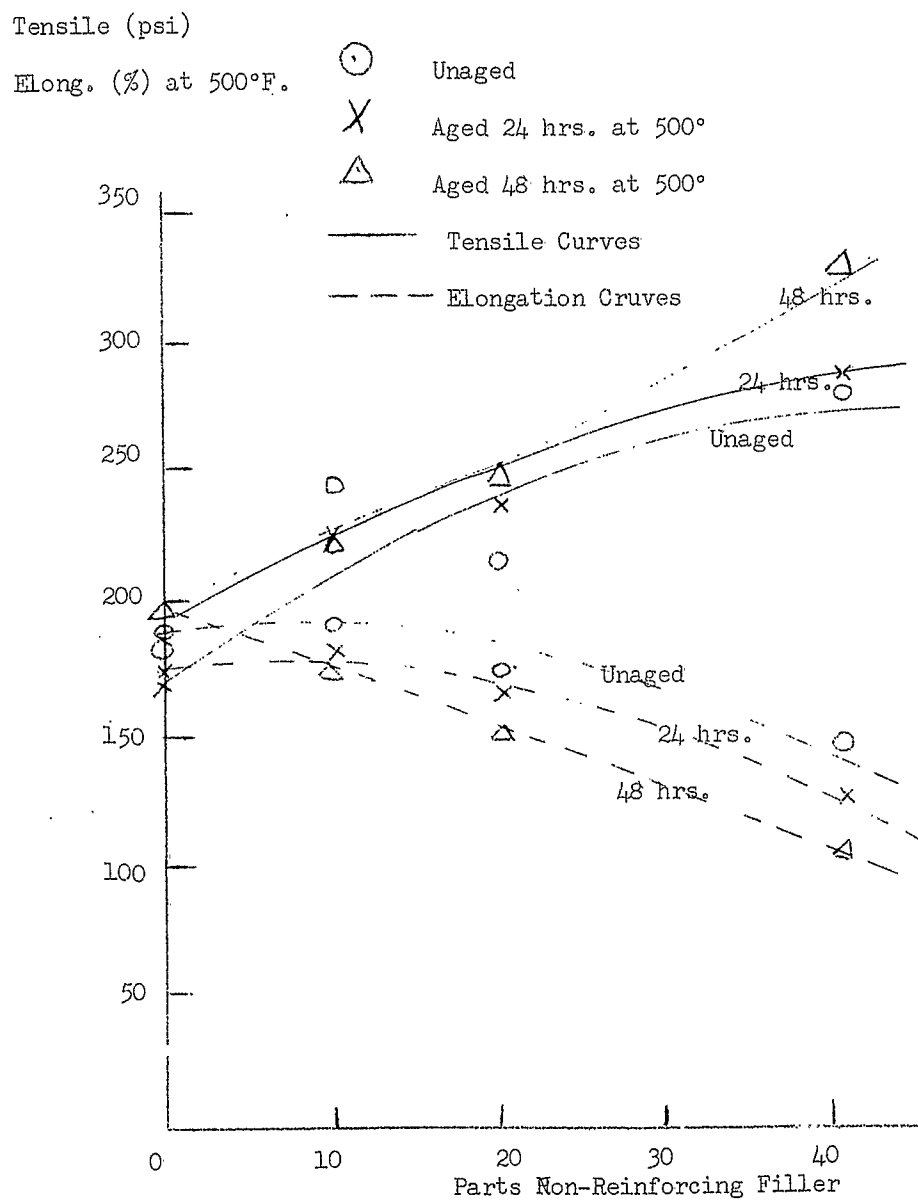


Figure 10 - Tensile and Elongation Data
Asbestine 625

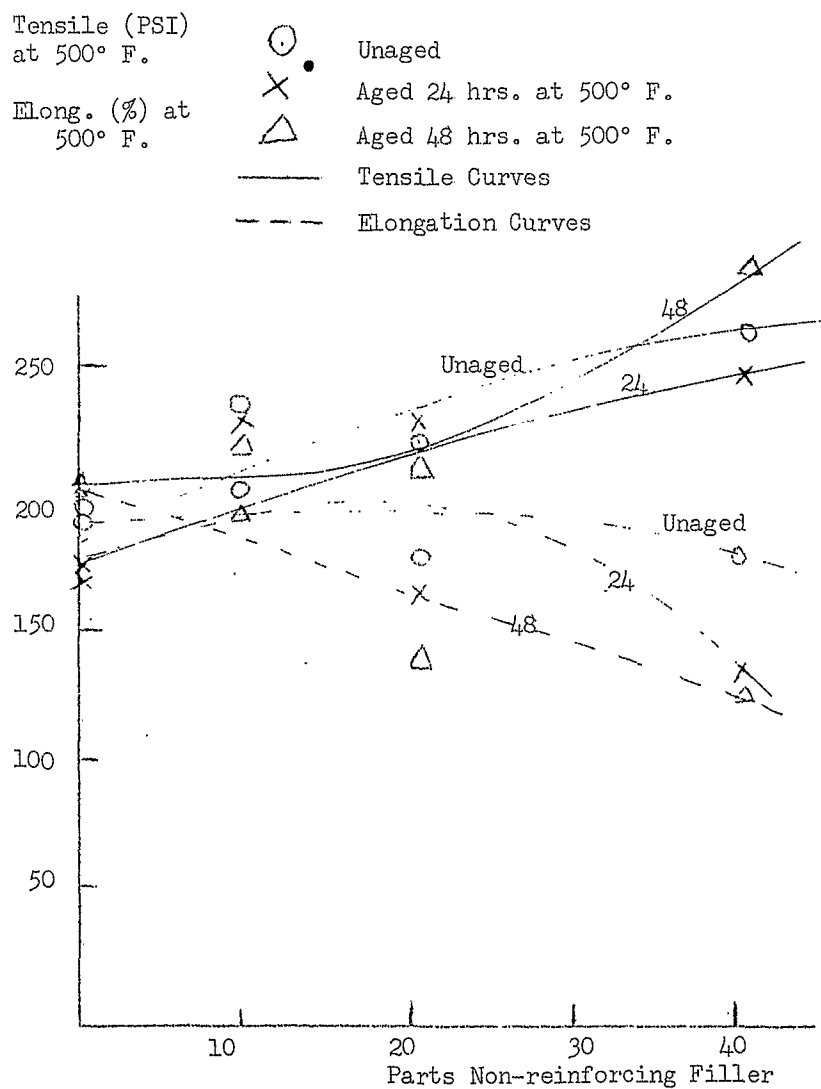
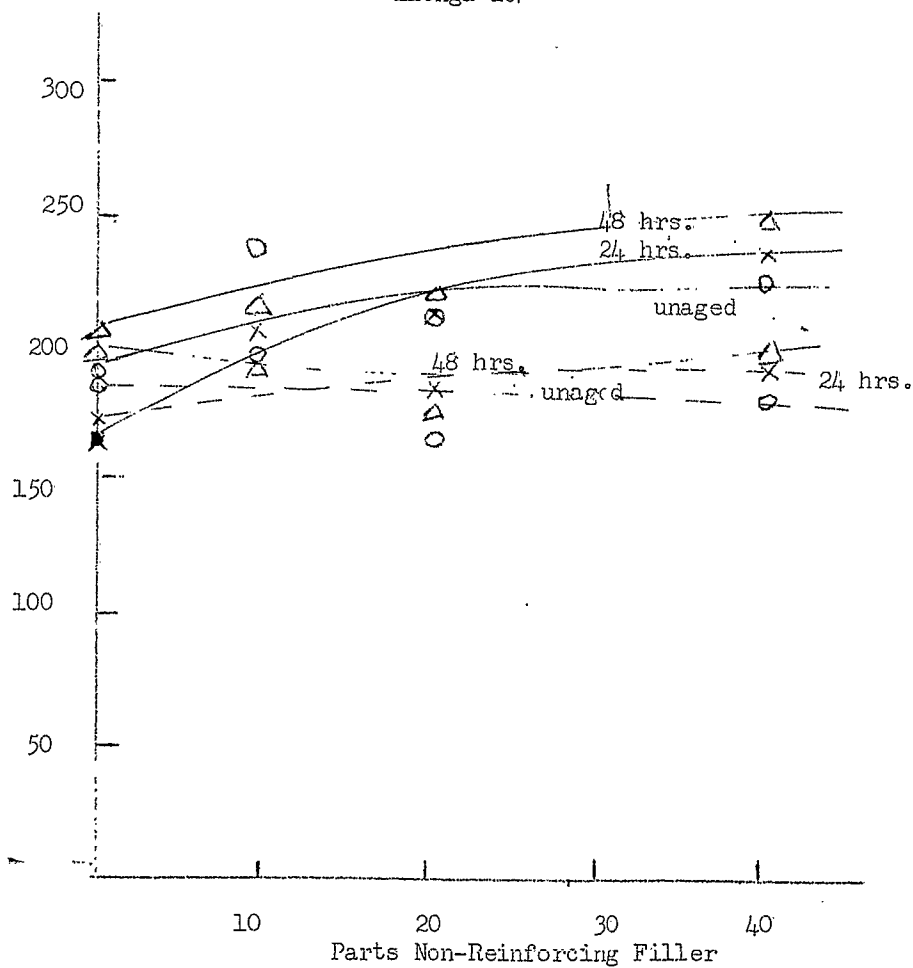


Figure 11 - Tensile and Elongation Data
Neo-Novacite

Tensile (psi)
at 500°

Elong. (%) at
500° F.

- Unaged
× Aged 24 hrs. at 500° F.
△ Aged 48 hrs. at 500° F.
— Tensile Curves
--- Elongation



4. Evaluation of Baymal Collodial Alumina

DuPont has on the market a collodial alumina with a specific surface area of $274^2\text{m} / \text{g}$, Baymal. It was compounded with silicone rubber in order to check its reinforcing properties. The alumina did not disperse properly. Agglomerated particles could be distinguished. The rubber was very weak after curing.

In view of the poor reinforcing action, it occurred to us that Baymal might be a substitute for the non-reinforcing filler. DuPont reports that the surface of each Baymal particle has been acetate-treated and that these groups may be removed by prolonged heating. Accordingly three samples were milled, each comprising 35 parts Quso 1841, Silastic 440, and 10 parts Baymal. The first sample was untreated Baymal, as received (this had a strong odor of acetic acid). The second and third samples comprised Baymal heated for 3 days at 300°C . and 425°C . respectively. Neither heated sample had any odor.

The results, shown in Table V, indicate that Baymal gives a rubber of low tensile and elongation, poor aging properties, and that removal of the acetate surface coating by heating is extremely detrimental. This may be explained on the basis of the partly ionic character of aluminum oxide. In view of the beneficial results obtained with talc, one can only speculate why alumina is detrimental to the rubber and why asbestos and talc (magnesium and silicon oxides plus metallic impurities) are beneficial. The further evaluation of Baymal did not seem to be justified in the light of this data.

Table V -- Evaluation of Baymal

Sample No. 354-	Description	Test Temp.	Tens- ile psi	Elong- ation %	50% Modu- lus	Hard- ness
5-B1	Sil. 440 + 35 Pts. Quso 1841 + 10 pts. Baymal (not Dried) Aged 24 hrs. at 500°	72 500 500	441 146 174	*327 110 95	150 92 121	62 - 70.5
5-B2	Same, with Baymal dried at 300°C " " " " " " " " Aged 24 hrs. at 500°	72 500 500	286 133 151	215 104 85	141 85 114	62 - 73.5
5-B3	Same, with Baymal dried at 425°C " " " " " " " " Aged 24 hrs. at 500°	72 500 500	72 41 58	40 38 52	- - -	48.5 - 62.5

5. Investigation of Vinylated Fillers

A rubber with a high tensile at 500° F. was considered of prime importance and some sacrifice in elongation was permitted to obtain this result. Some vinyl-modified fillers were re-examined with this in mind. An allyl-modified Cab-O-Sil was also checked again, but the rubber cracked during the curing period. It further decomposed during the postcuring at 480° F.

Hi-Sil 233 was reacted with 25 mole percent of the usual amount of vinyltrichlorosilane. The filler was only partially hydrophobic. It floated on the surface but wetted when shaken vigorously. A rubber sample compounded with this filler formed bubbles during the post-curing period at 480° F.

A similarly reacted filler with vinyl dimethylchlorosilane was very hydrophobic. The rubber sample compounded with this filler cured properly. In both the above cases the milling was very tedious. The compounds milled with sharp edges and crumbled. 2.5 pts. of diphenylsilanediol was added after which the milling was improved slightly. The sample compounded with the vinyl dimethyl-modified filler had a somewhat lower tensile than expected, only 139 psi at 500° F. Millings of filler modified with allyl trichlorosilane (305-87A) and vinyl trichlorosilane (253-104A) gave rubbers which showed evidence of cracking and decomposition during curing. Fillers modified with vinyl tris(2-methoxyethoxy) silane (305-70) and a mixture of vinyl dimethylchlorosilane and trimethylchlorosilane (253-109) cured properly but gave low tensiles (see Table VI).

Table VI - Evaluation of Vinyl-modified Fillers

Sample No.	Description	Test Temp.	Tensile	Elong.	50% Modul.	Hardness
110-1	SE-33 + 35 pts. 305-70 Filler * (vinyl trialkoxy-modified MS-5)	72	201	433	54	43.5
	Aged 24 hrs. at 500°	500	105	220	38	-
	Aged 24 hrs. at 500°	500	202	117	102	61.5
	Aged 48 hrs. at 500°	500	247	94	146	67.5
110-2	SE-33 + 35 pts. 305-87A Filler* (MS-5 modified with Allyl-SiCl ₃)	Very weak, cracked during curing				
110-5	SE-33 _ 45 parts 253-109 Filler* (Quso mod. with vinyl Me ₂ SiCl and Me ₂ SiCl)	72	557	555	78	52
	Aged 24 hrs. at 500°	500	180	247	47	-
	Aged 24 hrs. at 500°	500	154	241	42	51.5
	Aged 48 hrs. at 500°	500	166	243	45	56
107-2	SE-33 _ 35 pts. 253-105 Filler* (HiSi1 233 mod. with vinyl Me ₂ SiCl)	72	580	833	33	49
	+ 2.5 pts. $\phi_2\text{Si}(\text{OH})_2$	500	139	236	33	-
	Aged 24 hrs. at 500°	500	152	258	31	52
	Aged 48 hrs. at 500°	500	152	244	32	57

* Analytical Data:% ClIodine # (Wijs)

305-70

0.05

17.5

305-87A

0.13

19.2

253-109

0.24

7.8

These results are certainly not anticipated. However, it could be that the vinyl- and alkyl-trichlorosilanes resulted in modified fillers loaded with adsorbed HCl or chemically bound chlorine. Two samples were therefore compared to determine if this consideration were valid. In general, we have not been able to increase the tensile at high temperature with vinyl modified filler. High loading leads to rubber with low tensile at room temperature. The only interesting observation we believe should be followed further is that they do lead to good elongation after high temperature aging. The 253-109 filler (containing 0.24% chlorine) gave both a higher tensile and a higher elongation than the chlorine-free 305-70 filler.

6. Investigation of Titanium Compounds

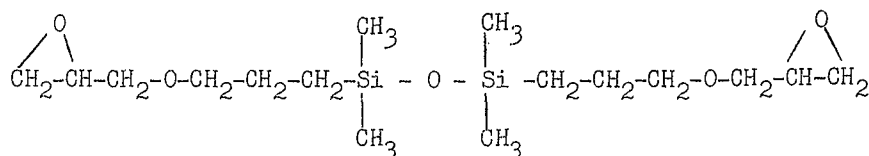
Previously, titanium dioxide was tested as a reinforcing filler and found to give a very weak rubber. We have now tested TiO_2 as a non-reinforcing filler (305-123-5B). Ten parts of TiO_2 milled with 35 parts of Quso gives a filler having slightly lower tensile at 500° F. than Asbestine 3X or Neo-Novacite. However, the tensile and elongation appear relatively unchanged upon 48 hours aging. This evaluation would be worth repeating at a higher loading of TiO_2 or perhaps a mixture of TiO_2 with Asbestine 3X. In this regard it is considered in the future that TiO_2 can be coated or reacted with a silane to give a hydrophobic filler (253-83).

A rubber sample milled with a silica filler which was modified with a tris-(trimethylsiloxy) titanium compound did not cure and formed

bubbles. The filler was very hydrophobic. It has been dried in vacuo at 150° C. It apparently reacted with the peroxide since no cross-linking occurred. The source of the bubbles is unknown since the filler was dried at a considerably higher temperature than the curing temperature, 115° C.

7. Other Additives

Ten parts of 1,3-bis[3(2,3-epoxypropoxy)propyl] tetramethyldisiloxane,



was added to a rubber recipe on the mill with the expectation that additional crosslinking will occur between the polymer ends and the silanol groups on the filler (it could also crosslink the filler particles- therefore it was added when the filler was milled in and dispersed through the rubber). The disiloxane reacted as a plasticizer. The elongation increased while the tensile decreased. (See Table VII)

Table VII Evaluation of "Epoxydisiloxane"

Sample No.	Description	Test Temp.	Ten-sile	Elong.	50% Modul.	Hardness
305-118-E	SE-33, 35 pts. Q-1841, 10 pts. "epoxydisiloxane"	72	525	869	60	48
		500	152	290	47	-
	aged 24 hrs., 500° F.	500	164	225	58	53
	aged 48 hrs., 500° F.	500	175	164	76	58

Abbr: Q = Quso

REFERENCES

1. Contract DA-36-034-ORD-3523 RD Study leading to the Development of Reinforced High Temperature Elastomers, June 1961 to September, 1962, work performed for Rock Island Arsenal, Rock Island, Illinois by The Borden Chemical Company, Central Research Laboratory, Philadelphia 24, Pa. (Dr. K. C. Tsou, Dr. S. Makower, Mr. R. N. Goldey, Dr. B. D. Halpern)
2. Kipping, F. S., J. Chem. Soc. 101, 2108 (1912)
3. Daudt, W. H. and J. F. Hyde, J. Am. Chem. Soc. 74, 386 (1952)
4. Dow Corning Data Sheet on Silastic S-2226
5. Gingold, K. and E. Rochaw, J. A. C. S. 76, 4852 (1945)